



Standard Test Method for Ferrous Iron in Iron Oxides¹

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1. Scope

1.1 This test method covers the quantitative determination of ferrous oxide (FeO) by oxidation of ferrous iron (Fe⁺⁺) in an acid solution to the ferric state (Fe⁺⁺⁺) and titration with potassium dichromate using diphenylamine as the indicator.

1.2 This test method is applicable to synthetic black iron oxide, natural black iron oxide, magnetite or brown iron oxide where part of the iron content is present in the ferrous state (Note 1). It is applicable to iron oxides where the ferrous iron content ranges from 50 to 0.20 %.

NOTE 1—Natural iron oxides and magnetite may contain traces of metallic iron that will be combined with and analyzed as FeO.

1.3 *This standard does not purport to address the safety concerns if any, problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

D50 Test Methods for Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese

D280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments

D769 Specification for Black Synthetic Iron Oxide

D1193 Specification for Reagent Water

D3722 Specification for Natural Red and Brown Iron Oxide Pigments

D3724 Specification for Synthetic Brown Iron Oxide Pigment

3. Significance and Use

3.1 This test method may be used for production quality control or specification acceptance.

4. Apparatus

4.1 The digestion apparatus consists of a standard 500-mL Erlenmeyer flask fitted with a two-hole rubber stopper and glass tubing, as shown in Fig. 1, to provide for the introduction of the inert gas and vent for gas and digestion fumes.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II of Specification D1193.

5.3 *Diphenylamine Indicator*—Dissolve 1 g of diphenylamine in 100 mL of concentrated (H₂SO₄) (sp gr 1.84).

5.4 *Hydrochloric Acid (1+1)*—Dilute concentrated hydrochloric acid (HCl, sp gr 1.19) with an equal volume of reagent water.

5.5 *Iron Ore, Standard, Sibley No. 27-f.*⁴

5.6 *Potassium Dichromate, Standard Solution (0.1 N)*—Dissolve 4.904 g of K₂Cr₂O₇ in water and dilute to 1 L. Standardize against National Institute of Standards and Technology standard sample No. 27f of Sibley iron ore. Calculate the Fe factor in grams per millilitre for the solution as:

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.31 on Pigment Specifications.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁴ May be secured from National Institute of Standards and Technology, Department of Commerce, Washington, DC 20234. Other recognized primary iron standard may be substituted.

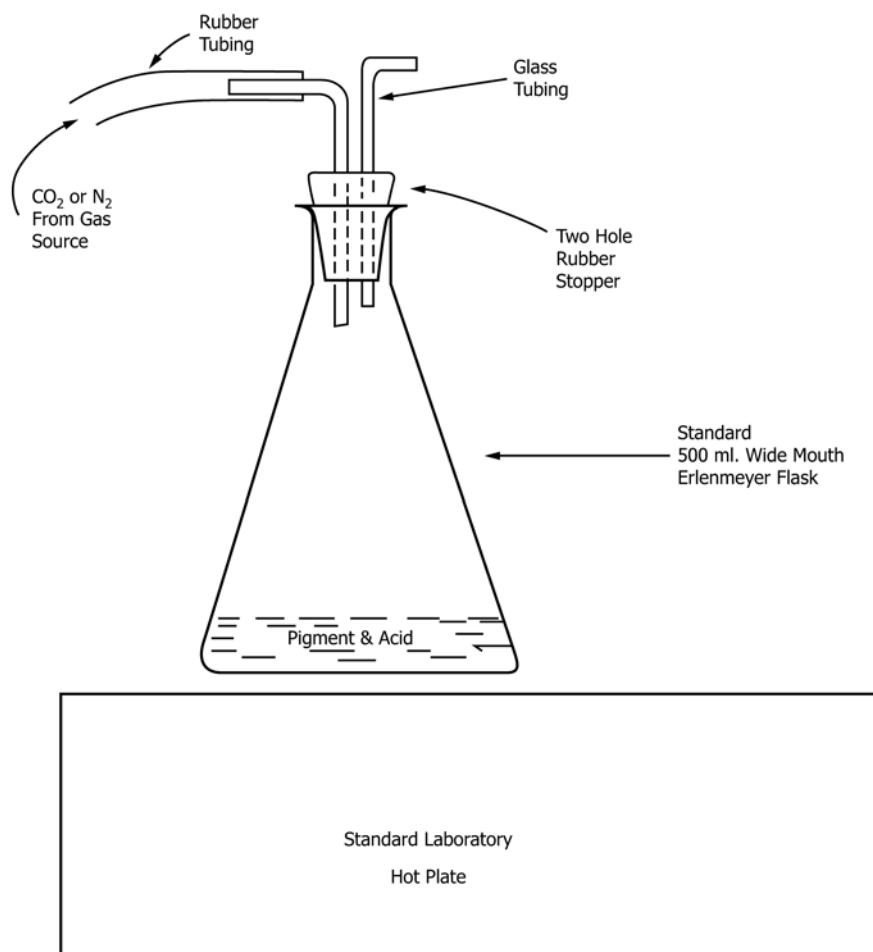


FIG. 1 Digestion Apparatus

$$Fe = W/V_1 \quad (1)$$

where:

W = weight of Fe in the standard iron ore (not the solution, as there is none), and

V_{V_1} = $K_2Cr_2O_7$ required for titration of standard, mL.

5.7 Sulfuric-Phosphoric Acid Solution—Prepare by carefully adding 600 mL of concentrated sulfuric acid (H_2SO_4) (sp gr 1.84) to 800 mL of water while stirring, then add 600 mL of phosphoric acid (85 to 87 %) mixing thoroughly. Cool and store.

6. Preparation of Sample (Note 2)

6.1 Mix the sample thoroughly and take a representative portion for the analysis. Exercise care at all times to prevent oxidation of the Fe^{++} iron to the Fe^{+++} state (Note 2). Grind natural iron oxides or natural magnetites to 100 % minus 100 mesh.

6.2 Finely divided synthetic black iron oxides if not carefully dried can oxidize so that part of the Fe^{++} iron is converted to Fe^{+++} . For this reason moisture should be determined on a separate specimen or by Test Methods D280, Part B. Vacuum drying at temperatures not exceeding 65°C is recommended.

NOTE 2—Coarsely ground natural iron oxides and magnetite are very

slow to dissolve. Exercise care in grinding oxides containing ferrous iron to avoid generating heat, as additional grinding could oxidize ferrous to ferric iron.

7. Procedure

7.1 Weigh 0.5 g of oxide to 1 mg and transfer to the 500-mL Erlenmeyer flask. Wash down the sides of the flask with 15 mL of water.

7.2 Attach the stopper with funnel and the gas delivery tube to the flask. Open the CO_2 valve until a gentle stream of gas flows through the flask. Nitrogen may be substituted.

7.3 Add 15 mL of 1 + 1 HCl (1+1). Digest on an asbestos pad on the hot plate at just below boiling temperature until completely dissolved or there is no further reaction (Note 3). Finely divided synthetic black or brown oxides usually require 5 to 10 min but natural oxides or magnetites may require considerably longer.

NOTE 3—Synthetic black iron oxides may contain small amounts of carbon black to increase tint strength. Carbon black will not dissolve during the digestion step and should not be confused with the soluble iron oxide.

7.4 Remove the flask from the hot plate and add 30 mL of sulfuric-phosphoric acid solution. Add 60 mL of water and cool in the water bath for 5 min.

7.5 Remove the CO₂ apparatus and add 5 drops of the diphenylamine indicator. Titrate with the standard potassium dichromate solution. The end point is sharp with a color change from green to purple. Avoid going past the end point.

8. Calculations

8.1 The percent FeO or Fe⁺⁺ in the unknown sample are calculated by using Eq 1 or Eq 2.

where:

W = weight of Fe in standard solution, g, and
 V = volume of potassium dichromate solution, mL.

$$\% \text{ FeO} = \frac{V \times F \times 1.2865 \times 100}{S} \quad (2)$$

where:

F = Fe factor defined by Eq 1, and
 S = specimen weight, g.

$$\% \text{ Fe}^{++} = \frac{V \times F \times 100}{S} \quad (3)$$

$$1.2865 = \frac{\text{molecular weight of FeO}}{\text{molecular weight of Fe}} = \frac{71.85}{55.847}$$

8.2 Report results to 0.1 %.

9. Precision and Bias

9.1 The precision statements are based on an interlaboratory study of the method in which operators in seven laboratories

analyzed in duplicate on two days two commercial synthetic black iron oxides containing 20 and 23 % ferrous iron oxide. The within-laboratory standard deviation was found to be 0.235 for the first material and 0.05 for the second, each with 7df. The between-laboratory standard deviations were 0.061 and 0.058, respectively, each with 6 df. Based on the pooled standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

9.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 0.5 % absolute at FeO contents of 20 to 25 %.

9.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.8 % absolute at FeO contents of 20 to 25 %.

9.2 *Bias*—Bias has not been determined.

10. Keywords

10.1 ferrous iron content; iron oxides; ferrous iron content; pigment; iron oxides

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